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RESONANTLY ENHANCED VACUUM ULTRAVIOLET GENERATION AND MULTIPHOTON IONIZATION IN CARBON MONOXIDE GAS*

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ABSTRACT

Competition between three-photon resonantly enhanced vacuum ultraviolet third-harmonic generation and six-photon multiphoton ionization using the A state in gaseous carbon monoxide is observed. Excitation spectra of the third-harmonic emission exhibit increasing blue shifts and broadening with increasing pressure due to the phase matching requirements. Estimates for the efficiency and tunability show that third-harmonic generation in carbon monoxide molecules is a promising source for coherent vacuum ultraviolet light.

INTRODUCTION

The attraction of using molecular vapors as a nonlinear medium to generate vacuum ultraviolet (VUV) radiation has recently been reviewed by Wallace.[1] Despite the convenience of having a fixed gas for the nonlinear medium, single frequency pump sources, and wide tunability due to the width and number of molecular vibronic bands, only one detailed account of third-harmonic generation (THG) in molecules has been published.[2] In that study, two and three-photon resonantly enhanced THG in nitric oxide was reported. We report the observation of three-photon resonantly enhanced THG through the $A^1\Pi$ - $X^1\Sigma$ transition (fourth positive system) of carbon monoxide (CO) gas. In addition to detecting VUV radiation we simultaneously record signals from $A^1\Pi$-resonantly enhanced six-photon multiphoton ionization (MPI). Results of such studies in xenon[3,4] have shown that THG and MPI can be competitive processes. We report similar findings where it is observed that signals due to MPI disappear at wavelengths to the blue of the R-head in the CO A state and, concurrently, intense VUV third-harmonic radiation is detected in the forward direction.

Despite the fact that nonresonant THG in CO has failed in the past,[5] it was chosen in the present study for a number of reasons. It is a gaseous material and processes competing with third-harmonic emission are suppressed. Its high ionization potential (14.01 eV)[6] and high dissociation limit (11.11 eV)[7] make these two processes higher order and therefore unlikely in the wavelength region of interest. Furthermore, it was felt that by using the resonant enhancement due to the strong transition dipole of the A state,[8] an efficient VUV radiation source could be produced using powerful dye-laser pump sources. Finally, the extensive Franck-Condon envelope of this transition provides a wide tuning range.

*Work performed under the auspices of the US DOE.

EXPERIMENTAL

The experimental apparatus, shown in Fig. 1, is similar to that used by Miller et al.[3] It consists of a four-way cross connected to a vacuum system. The output of a frequency-tripled Nd:YAG laser (Quanta-Ray DCR-1) pumped Coumarin 440 dye laser (Quanta-Ray PDL-1) is focused by either a 75- or 100-mm focal length lens to a waist calculated to be about 10 μm. The laser flux in the focal volume was on the order of 10^{29}-10^{30} photons $cm^{-1}s^{-1}$. Photoelectrons resulting from the MPI process are monitored with a flat-plate platinum collector. Amplification occurs by an electron avalanche in the CO gas due to a negative bias of 200-300 V on the other platinum plate. Vacuum UV radiation can pass through a LiF window into a differentially pumped five-way cross filled with argon counting gas at 0.5 Torr. If VUV light strikes the negatively biased tantalum foil, the ejected photoelectrons are collected with another flat-plate platinum electrode. The tantalum foil (work function 4.2 eV) is angled, which enhances its yield for photoelectrons.[7] A VUV bandpass filter (Acton) is used to suppress background signals due to pump laser photons hitting the tantalum foil detector. The electron signals due to MPI are amplified (PAR 115) and integrated by a boxcar averager (PAR 162/164) before being recorded on an x-y plotter. Spectral grade CO (Matheson) is condensed at 77 K prior to use, suppressing intense interfering MPI signals due to trace carbonyl compounds[10,11] which have negligible vapor pressures at this temperature.

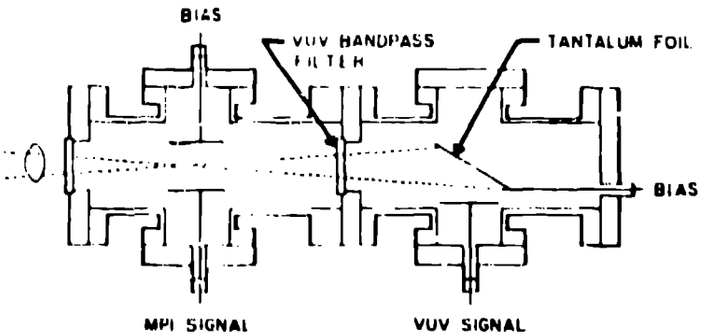

Fig. 1. Schematic diagram of the experimental apparatus used to measure the MPI and third-harmonic VUV radiation. The pump laser can also be positioned at 90° with respect to the detector.

THIRD HARMONIC GENERATION AND MULTIPHOTON IONIZATION

Figure 2 shows the MPI and THG excitation spectra for the $v' = 1$ and $v' = 2$ vibronic levels of the A state at a CO pressure of 10 Torr. The ionization signals are due to three-photon $A^1\Pi$ resonantly enhanced six-photon MPI. The signals at slower laser wavelength scan

speeds show the anticipated rotational structure.[6] To the blue of the R-head, ionization signals can no longer be detected, and only signals due to VUV radiation are observed. The VUV light is only detected in the forward direction with respect to the pump laser. The excitation spectrum exhibits increasing blue shifts and bandwidths with increasing pressure. This is shown in Fig. 3. Also apparent in Fig. 3 are sharp dips in the VUV signal due to absorption by e $^3\Sigma^-$ (v'=4) rovibronic levels in CO,[6] confirming identification of the VUV light as tunable monochromatic third-harmonic emission. To account for similar MPI-THG phenomena in xenon, a two-level model has been used.[4] This two-level model involves coherent excitation of a group of atoms resulting in a collection of coupled dipoles which emit to the ground state with an enhanced oscillator strength. Qualitatively, the Rabi frequency of the three-photon pumping to the $A^1\Pi$ level and the Rabi frequency of the stimulated emission to the ground state are coupled.

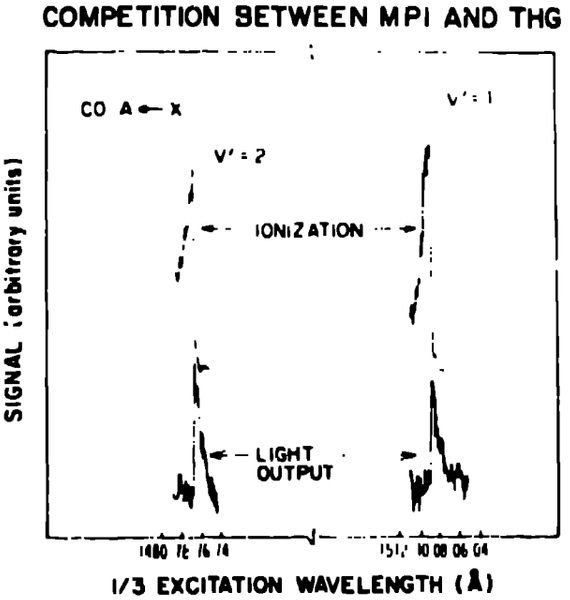

Fig. 2. The MPI and THG excitation spectra of the $^1\Pi$ v' = 1 and v' = 2 vibronic levels in CO at a pressure of 10 Torr. At slower dye laser wavelength scan rates the individual CO rotational lines are apparent in the MPI spectrum.

The blue shifts and broadening of the VUV light with pressure are consistent with the wave vector phase matching requirements.[12, 13] The phase mismatch Δk may be written as

$$\Delta k = 6\pi\,(n_p - n_{TH})/\lambda_p \qquad (1)$$

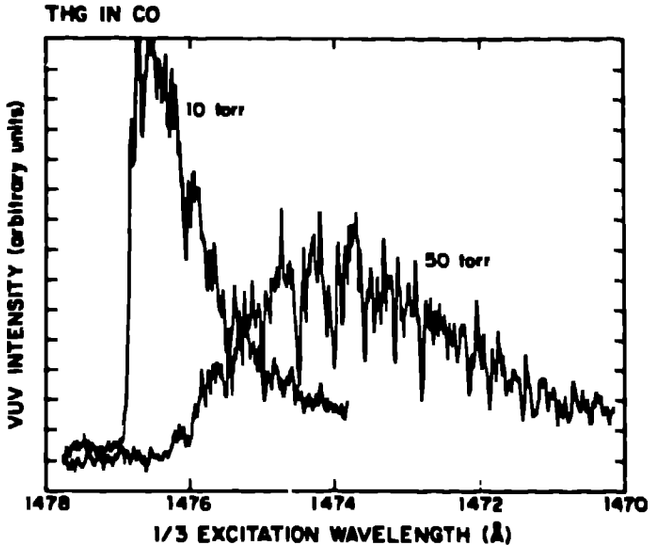

Fig. 3. Excitation spectra of the third-harmonic emission in the $^1\Pi$ v' = 2 level of CO at pressures of 10 and 50 Torr. The sharp dips in the VUV emission are due to self absorption by rovibronic levels in the e $^3\Sigma^-$ (v'=4) band of carbon monoxide.

where λ_p is the dye laser pump wavelength, and n_p and n_{TH} are the refractive indices at λ_p and $\lambda_p/3$ respectively. Bjorklund[13] has shown that the optimum phase mismatch for focused beams has a small negative value. In CO the generated VUV frequency is higher than that of the vibronic levels of the A state, and, therefore, the anomalous dispersion makes a negative Δk possible.

Measurements of the maximum THG output of CO and Xe show that they are comparable. The efficiency for THG in Xe has been previously reported.[14] It is important to note that the efficiency for THG goes as the square of the pump laser flux, thus increased THG efficiency should be possible by raising the laser flux to the limit of dielectric breakdown. We observed that this limit is noticeably higher in CO than Xe. Also, the higher $^1\Pi$ vibronic levels up to the predissociation limit exhibit third-harmonic emission, and tuning in the 1300-1500 Å wavelength region is observed as shown in Fig. 4.

Ongoing experiments are exploring the use of CO as a nonlinear medium to generate VUV radiation in the Lyman-alpha wavelength region. The v'=14 level of ^{13}CO is ideally suited for this purpose. Using an injection-locked XeCl laser as a source of 308 nm radiation, which is a near two-photon A $^1\Pi$ (v'=0) resonance, together with 578 nm Rhodamine or copper vapor laser photons, a powerful 1216 Å source appears feasible.

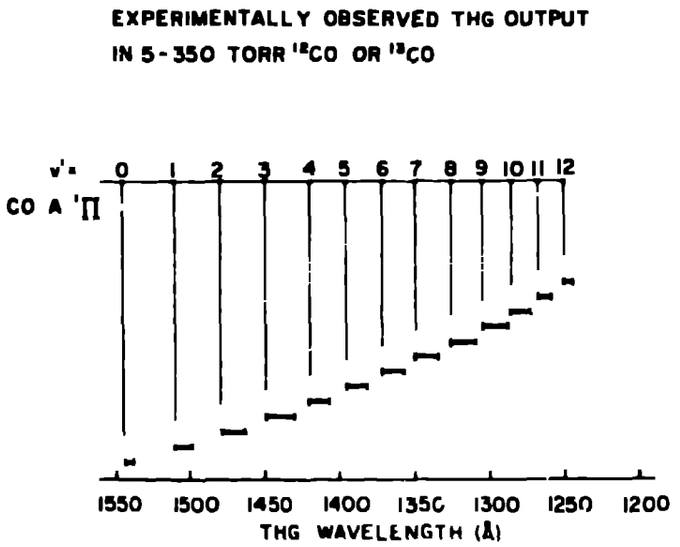

Fig. 4. Wavelengths for which third-harmonic radiation has been observed in $C^{12}O^{16}$ and for which third-harmonic should be observed in $C^{13}O^{16}$ using a single dye laser as an excitation source.

SUMMARY

In summary, it has been shown that CO vapor can be used to generate coherent tunable VUV radiation by THG using a single tunable dye laser. By simultaneously recording MPI and THG, it is found that these are competitive processes. The shifts to higher frequencies and the broadening of the third-harmonic emission with increasing CO pressure are found to be due to the phase matching requirements.

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